

CATALYST FOR THE PRODUCTION OF LIGHT OLEFINS

CROSS REFERENCE TO RELATED APPLICATION

5 This application claims priority from U.S. Patent Application No. 60/407,223, filed August 29, 2002.

BACKGROUND OF THE INVENTION

10 Field of the Invention

 The present invention is related to the catalytic production of light olefins.

Prior Art

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 In recent years, there has been a tendency to utilize the fluid catalytic cracking process, not as a gasoline producer, but as a process to make light olefins for use as petrochemical materials or as building blocks for gasoline blending components, such as MTBE and alkylate.

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 The traditional method for the production of light olefins, such as ethylene, propylene, and butylene, from petroleum hydrocarbon is tubular furnace pyrolysis or pyrolysis over heat carrier or by catalytic conversion of lower aliphatic alcohol. More recently, the fluid catalytic cracking process employing small pore zeolite additives from the pentasil family is being used for the same at modern refinery. The small pore zeolite additives can be prepared as described in several patents (e.g. US 5, 472, 594, or

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WO98/41595).

 Further descriptions of the production of light olefins by cracking processes are

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given in US Pat. No. 3,541,179; and JP No. 60-222 428.

 The small pore zeolite additives are applied at the refinery by blending with the FCC host catalyst typically at 1-5 wt-% concentration. The obtained light olefin increase depends on the effectiveness of the additive, on the base catalyst formulation, feed type, and FCC

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process conditions, such as residence time and temperature. However, if the refiner targets a light olefin concentration, which is higher than that obtained at 1-5 wt-% intake of the

small pore zeolite additive, usually the overall performance will start to deteriorate. This is because of a dilution of the host catalyst and increase in the bottoms conversion and saturation of the light olefins yield.

5 SUMMARY OF THE INVENTION

In one embodiment, the present invention is a catalyst composition comprising a pentasil type of zeolite, one or more solid acidic promoters and, optionally, a filler and/or binder.

10 In a second embodiment, the present invention is a method of making the above catalyst composition, wherein an aqueous slurry comprising the pentasil-type zeolite and solid acidic cracking promoter is prepared and dried.

In a third embodiment, the present invention is a process for producing olefins
15 having up to about 6 carbon atoms per molecule, comprising contacting a petroleum feedstock at fluid catalytic cracking conditions with the above catalyst composition.

Other embodiments of the invention relate to details concerning catalyst composition, making the catalyst composition and use of the composition in making olefins.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention describes FCC catalyst and catalyst/additive systems, which can be used to produce higher concentrations of olefins, particularly propylene, than obtained with the conventional additive systems as described above, and at the same time
25 achieving high bottoms conversion. The systems are designed to function also in the processing of heavier feeds, which are especially sensitive to the dilution effects when using the conventional catalyst/additive systems at higher additive concentrations. The systems of this invention do not suffer from the dilution of the active ingredients and deterioration of the overall performance.

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The acidic zeolite materials may be selected from the group consisting of mordenite, zeolite Beta, NaY zeolite and USY zeolite that is dealuminated or ion exchanged with transition metals or both. The preferred transition metal is vanadium.

5 In the catalyst composition of the invention, the solid acidic cracking promoter may comprise a co-gel of alumina-aluminum-phosphate or aluminum phosphate that has been doped with an acidic compound.

10 The catalyst composition of the invention may comprise one or more additional materials selected from the group consisting of particle binders, diluents, fillers and extenders. The pentasil-type zeolite is a pentasil type of zeolite may comprise from about 5.0 wt% to about 80 wt% of the composition. The composition may comprise particles having average lengths along their major axis of from about 30 microns to about 150 microns.

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The weight ratio of said pentasil-type zeolite to solid acidic cracking promoter in the catalyst composition of the invention may be from about 0.03 to about 9.0.

20 The solid acidic cracking promoter in the composition may comprise from about 5.0 wt% to about 80 wt% of the composition.

The catalyst composition of the invention may comprise particles having average lengths along their major axis of from about 20 microns to about 200 microns.

25 The Modified Forms of Pentasil-Type Zeolite

For clarity and simplicity, and to distinguish from the ZSMs known in the art, the modified pentasil zeolites, prepared according to this invention are identified as MPZ- (ZSMs). For example, some of the types of pentasil zeolites used in the invention involve, but are not limited to, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, zeolite beta, zeolite boron beta, which are described in U.S. Patents Nos. 3,308,069; 3,702,886;

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3,709,979; 3,832,449; 4,016,245; 4,788,169; 3,941,871; 5,013,537; 4,851,602; 4,564,511;
 5,137,706; 4,962,266; 4,329,328; 5,354,719; 5,365,002; 5,064,793; 5,409,685; 5,466,432;
 4,968,650; 5,158,757; 5,273,737; 4,935,561; 4,299,808; 4,405,502; 4,363,718; 4,732,747;
 4,828,812; 5,466,835; 5,374,747; 5,354,875; incorporated herein by reference. Metals in
 5 tetrahedra coordination in the zeolite crystals include: AL, AS, B, Be, Co, Cr, Fe, Ga, Hf, In,
 Mg, Mn, Ni, P, Si, Ti, V, Zn, Zr.

Modified forms of pentasil-type zeolites (here and after referred to as MPZs) such as
 ZSMs, Beta and so on, briefly involve doping said zeolites with metal ions such as, but not
 10 limited to alkaline earth, transition metals, rare earth metals, phosphorous, boron, aluminum.
 The MPZ zeolites can be mixed with regular pentasil zeolites (i.e., ZSM, Beta, etc.) or with
 ion exchanged forms of pentasil zeolites, known to present state of the art such as pentasil
 zeolites exchanged with transition metals.

15 The pentasil zeolite may be doped with a compound comprising a metal ion selected
 from the group consisting of ions of alkaline earth metals, transition metals, rare earth
 metals, phosphorous, boron, aluminum, noble metals and combinations thereof. The
 pentasil-type zeolite may be doped by any of the following methods:

- ion exchange with the metal ion;
- 20 • use of doped seeds;
- use of doped reactants;
- use of seeds comprising X- or Y-type zeolites that have never been ion
 exchanged with the metal ion;
- incorporating salts comprising the metal ion in a reaction mixture comprising the
 25 precursor of the pentasil-type zeolite.

Making the Catalyst of the Invention

In making the catalyst composition of the invention an aqueous slurry comprising a
 pentasil-type zeolite and solid acidic cracking promoter is prepared and dried. Separate
 30 aqueous slurries of the pentasil-type zeolite and solid acidic cracking promoter may be

prepared, mixed together and dried. The aqueous slurry may be spray dried to obtain catalyst particles having average lengths along their major axis of from about 40 microns to about 100 microns.

5 The catalyst composition of the invention may comprise one or more additional materials selected from the group consisting of particle binders, diluents, fillers and extenders. This may be made by modifying pentasil-type zeolite by ion exchange with ions selected from the group consisting of ions of alkaline earth metals, transition metals, rare earth metals, phosphorous, boron, aluminum, noble metals and combinations thereof,
10 preparing an aqueous slurry of acidic cracking promoter and other catalyst ingredients other than the modified pentasil-type zeolite, adding the modified pentasil-type zeolite to the slurry and shaping the slurry, the addition of the modified pentasil-type zeolite being carried out as a final step immediately prior to shaping. The addition of the modified pentasil-type zeolite may be carried out by mixing with the aqueous slurry until the slurry is substantially
15 homogeneous. Shaping may be carried out by spray drying.

NH_4OH may be added to the slurry prior to the addition of the modified pentasil-type zeolite to raise the pH of the slurry. A pH buffer may be added to the slurry prior to the addition of the modified pentasil-type zeolite. The buffer may be selected from the group
20 consisting of aluminum chlorohydrol, phosphate sol or gel, anionic clay, smectite and thermally or chemically modified clay. The thermally or chemically modified clay may be kaolin clay.

 An aqueous slurry may be prepared comprising solid acidic cracking promoter and
25 precursors of the pentasil-type zeolite comprising silica, alumina and seeds containing one or more metals from the group consisting of rare earth metals, alkaline earth metals and transition group metals, forming the aqueous slurry into shaped bodies and crystallizing the pentasil-type zeolite in situ in the shaped body.

catalytic cracking conditions, typically comprising a temperature from about 450-780°C, residence time from about 0.01 to 20 seconds, with and without added steam, and a catalyst-to-oil ratio from 1 to 100. The catalyst composition may comprise about 5.0 to about 80 wt% of a mixture of the catalyst composition of the invention and a second
 5 fluidized catalytic cracking catalyst composition.

The pentasil zeolites used in the following examples were synthesized and modified with various metals and phosphorous as described above.

10 EXAMPLES

Comparative example 1:

Commercially available ZSM-5 additive (65 wt.% pseudo boehmite alumina and 35 wt.% ZSM-5 zeolite) was calcined and blended with a base catalyst of a formulation 34 wt-
 15 % Y zeolite (Re/Y)=2, 13 wt-% (pseudoboehmite) alumina, 12 wt-% binder, and clay to balance. The amount of additive in the blend was 10 wt-%. Absent from the blend was a solid acidic cracking promoter.

Comparative example 2:

20 ZSM-5 was mixed with H₃PO₄ solution at pH <3, dried, and calcined at 600°C for 1 hr. The resulting zeolite (15 wt-% P₂O₅) was milled and embedded into a slurry of a peptized (pseudo boehmite) alumina and clay. The slurry was mixed with high shear, dried, and calcined. The final composition was 15 wt-% ZSM-5, 65 wt-% Al₂O₃, and 10 wt-% clay. Also absent from this blend was a solid acidic cracking promoter.

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Example 3:

Example 1 was repeated, but instead of 65 wt-% of (pseudo boehmite), alumina in the additive, an acidic cracking promoter of 15 wt-% deeply stabilized, low sodium USY and 15 wt-% modified (pseudo boehmite) alumina was employed. The modified (pseudo
 30 boehmite) alumina was prepared by adding 975 g phosphoric acid and 5823 g ReCl₃ (Rare Earth) solution to a heel of H₂O. Under stirring, 13700 g Natal (25 wt-% Al₂O₃) and

10172 g sulphuric acid was added at a fixed pH of 9.5 into the mixture. The slurry was aged at 100°C for 24 h, filtrated, washed, dried, and calcined.

5 A summary of catalyst properties and performance for the above Examples is given in the following Table:

Table of catalyst properties and performance

	E1 Comparative example	E2 Comparative example	E3
ABD	0.82	Na	0.72
SA BET	257	Na	231
Al2O3	73.1	Na	36.16
Re2O3	<0.1	Na	6.79
P2O5	1.89	Na	4.67
Conversion	63.4	76.0	78.3
Propylene	10.2	11.1	13.3
Butylenes	8.9	9.4	10.8
Gasoline	26.3	36.5	34.5
Bottoms	18.4	9.1	7.9

¹Small scale fluidized bed reactor at 540°C. Feed was a long residue with a CCR of 3.2

10 As is clear from the Table, use of the composition of the invention results in a marked increase in the yield of olefins as compared to use of a conventional composition.